Advanced Spectroscopic Techniques for the Analysis of Illicit Drugs and Explosives

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Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all the information sources and literature used are indicated in the thesis.

Adriano De Grazia

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Abbreviations

ABF	Australian Border Force
ADA	anthracene-2,3-dicarboxaldehyde
AFP	Australian Federal Police
ALS	alternating least squares
ATR	attenuated total reflection
CORCONDIA	core consistency diagnostic
2,4-DAT	2,4-diaminotoluene
2,6-DAT	2,6-diaminotoluene
DMS	dimethylsulfone
2,4-DNT	2,4-dinitrotoluene
2,6-DNT	2,6-dinitrotoluene
DOM	dissolved organic matter
DPMA	diphenylmaleic anhydride
EEM	excitation emission matrix
EMSC	extended multiplicative scatter correction
FPA	focal plane array
FTIR	Fourier transform infrared
GC-ECD	gas chromatography electron capture detector
GC-MS	gas chromatography mass spectrometry
GC-TEA	gas chromatography thermal energy analyser
GUI	graphical user interface
HPLC-DA	high pressure liquid chromatography diode array
HPLC-UV	high pressure liquid chromatography ultra violet
IDDR	Illicit drug data report
IED	improvised explosive device
IMS	ion mobility spectrometry
IR	infrared

LC-MS	liquid chromatography mass spectrometry
LEA	law enforcement agency
MCC	microcrystalline cellulose
MCR	multivariate curve resolution
MS	mass spectrometry
MSC	multiplicative scatter correction
NDA	naphthalene-2,3-dicarboxaldehyde
NIR	near infrared
NMR	nuclear magnetic reasonance
NPS	new psychoavtice substances
OPA	*o*-phthalaldehyde
PARAFAC	parallel factor analysis
PCA	principal components analysis
PEA	phenylethylamine hydrochloride
PETN	pentaerythritol tetranitrate
PIDI	preliminary illicit drug identification
RDX	cyclotrimethylenetrinitramine (research development explosive)
SAM	spectral angle mapper
SERS	surface enhanced raman spectroscopy
SFF	spectral feature fitting
SIMPLISMA	simple-to-use interactive self-modelling mixture analysis
TAT	2,4,6-triaminotoluene
TLC	thin layer chromatography
TNT	2,4,6-trinitrotoluene
TOF-MS	time of flight mass spectrometry

Abstract

Law enforcement agencies are on a path to intelligence-led-policing, with an aim of gaining as much information as possible and interpreting that into actionable intelligence as quickly as possible. The focus on this information is not necessarily how accurate it is, but in what intelligence it can provide. In the illicit drugs environment, information about mixtures and purity could take months to obtain under current procedures. In the field of explosives analysis there is always a need for field- deployable methodologies that do not require the acquisition of expensive equipment.

Currently available spectroscopic techniques used for the preliminary identification of illicit drugs are limited to "single point" spectroscopic methods. Samples that can prove particularly problematic for these methods include drug mixtures, especially those of low purity (e.g. tablets or powders with a range of diluents, adulterants and cutting agents) or new psychoactive substances (NPS) that have not previously been encountered. Furthermore, the information that these methods provide offers little value in the realm of intelligence to policing organisations. In a move to intelligence-led-policing and the desire for more data, ATR-FTIR hyperspectral imaging and Raman mapping are two techniques that have the potential to rapidly provide law enforcement with actionable intelligence on potential illicit drug samples. Both of these methods have been shown to have superior information content in comparison to their single point equivalents. This research compares the performance of the unsupervised chemometric techniques multivariate curve resolution (MCR) and simple-to-use interactive self-modelling mixture analysis (SIMPLISMA) in identifying components of mixtures (from hyperspectral image data) and estimating their purity, without the need for calibration. While all of the hyperspectral methods provided more information than current techniques, Raman mapping coupled with analysis by MCR was found to provide the most precise and accurate results.

A feasibility study on the analysis of nitroaromatic explosives via fluorescence landscapes and PARAFAC was conducted. Although the initial aim of the project was to determine a field-deployable, 'one-size-fits-all' approach to nitro-containing explosives detection via reduction to amines, the reduction method was only found to be suitable for nitroaromatic explosives. Following the reduction to amines, derivatisation with *o*-phthalaldehyde (OPA) was performed to form fluorescent isoindoles. This two-step derivatisation process was demonstrated to take less than 60 minutes and was assessed to be field-deployable. However, fluorescence landscapes of the derivatised amines were found to be too similar for PARAFAC to separate and quantify.